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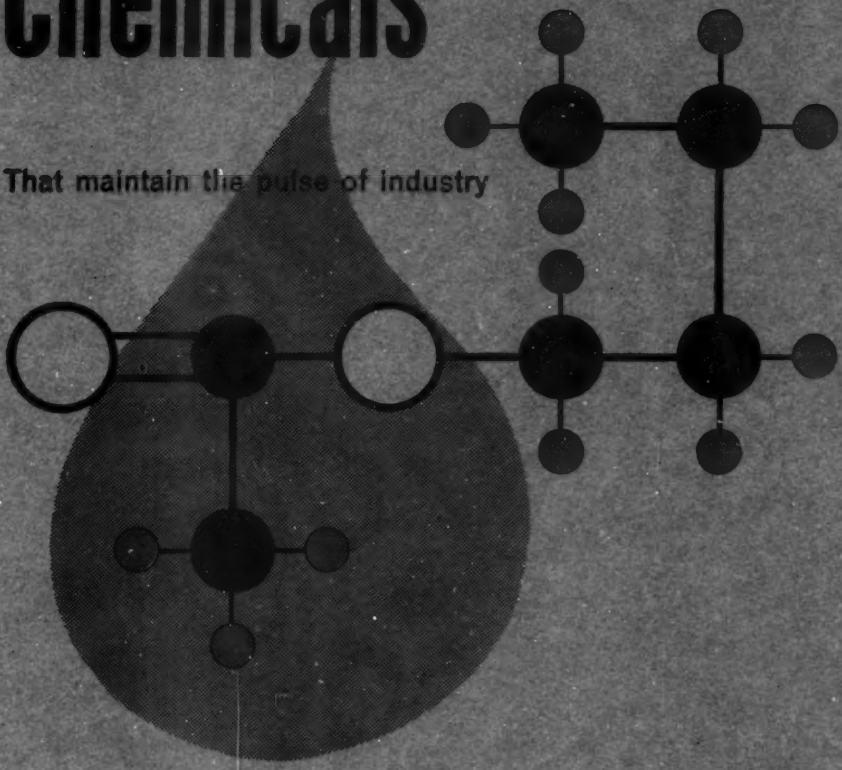

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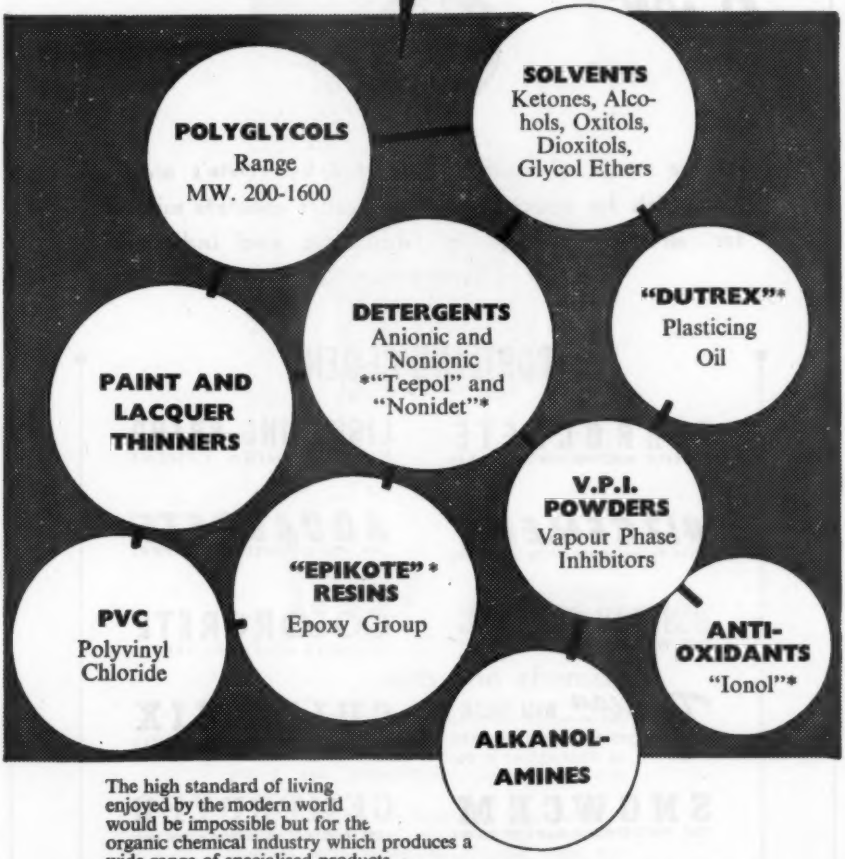

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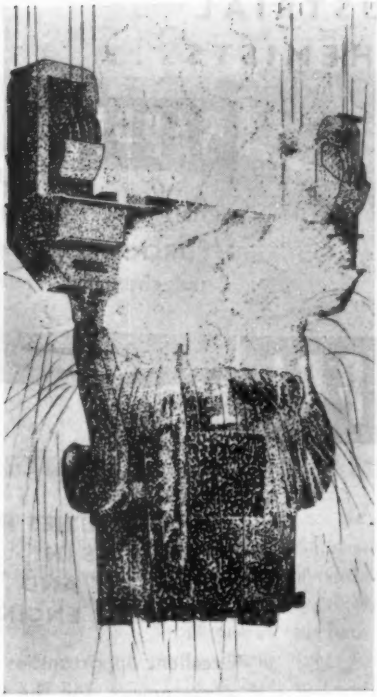

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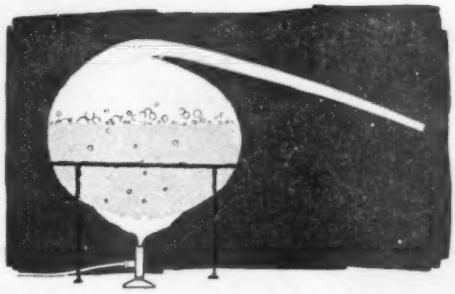

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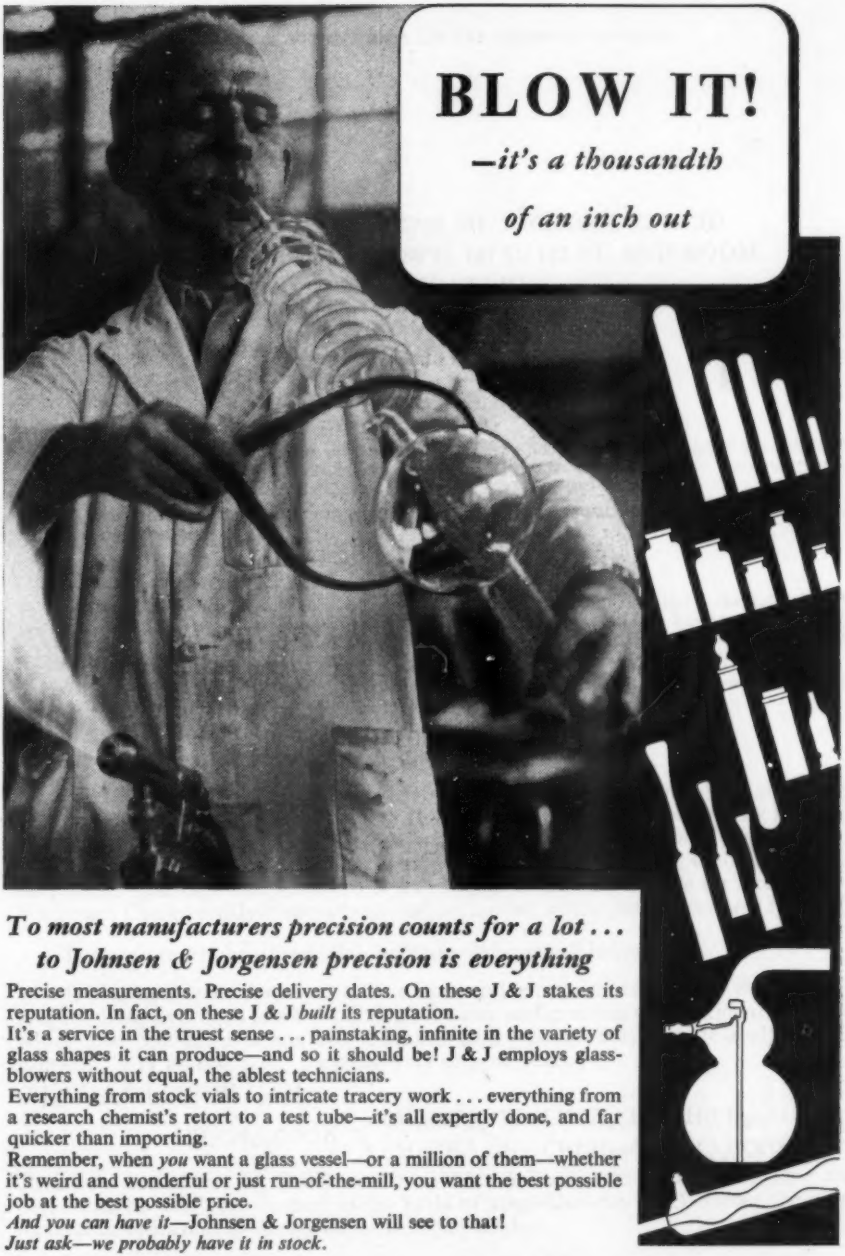

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THE AUTO-REACTIONS OF RICINOLEIC ACID PART I. REACTIONS AT 180°C, 147°C, 122·3°C AND ROOM TEMPERATURE

by

F. HAWKE and E. A. KOHLL

OPSOMMING

As risinoleïesuur onder 'n trae gas verhit word, is die hoofreaksie die vorming van estoliede. Die reaksie is van die tweede orde en die snelheidskonstante is bereken. Die molekulêrgewig-distribusie is bereken deur toepassing van die wette van polykondensasie.

Wanneer risinoleïesuur toegelaat word om by kamertemperatuur te staan is die hoofreaksie weer estoliedformasie.

SUMMARY

When ricinoleic acid is heated in an inert atmosphere, the main reaction is the formation of estolides. The reactions are of the second order, and the velocity constants have been claculated. The molecular weight distribution of the product has been calculated from the laws of polycondensation.

When ricinoleic acid is allowed to stand at room temperature, the main reaction is again estolide formation.

INTRODUCTION

Ricinoleic acid (12-hydroxyoctadec-9-enoic acid), in the form of its glycerides, is the major component of castor oil[1, 2]. It was first isolated in a pure state by Hawke[3], and its synthesis has been reported recently[4, 5, 6]. Brown and Green[7] and Hawke[3], amongst others, have noted that pure ricinoleic acid is very reactive; there is a marked drop in its hydroxyl value if it is left standing at room temperature for more than a few hours. Consequently it must be stored, as a solid, at temperatures lower than 4°C.

The auto-reactions of ricinoleic acid are summarised below:

1. *Intramolecular dehydration.* The hydroxyl group can react with either of the neighbouring hydrogen atoms, splitting off water and creating an additional ethylenic bond. The product is a mixture of linoleic acid (octadec-9:12-dienoic acid) and the isomeric "9,11 linoleic acid" (octadec-9:11-dienoic acid).

$$CH_3(CH_2)_4CH_2CHOHCH_2CH=CH(CH_2)_7COOH \begin{cases} \nearrow CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH \\ \searrow CH_3(CH_2)_5CH=CHCH=CH(CH_2)_7COOH \end{cases}$$

Research carried out by Priest and von Mikusch[2] indicates that linoleic acid and "9,11 linoleic acid" are formed in the ratio of approximately 2·5:1 during the commercial dehydration of castor oil or its fatty acids.

2. *Intermolecular dehydration.* The hydroxyl group can condense with a free carboxyl group of another molecule, forming estolides. The reaction can be repeated, yielding long-chain polycondensates.

$$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOH + HO\underset{\displaystyle (CH_2)_5CH_3}{\underset{|}{C}}HCH_2CH{=}CH(CH_2)_7COOH \rightarrow$$

$$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COO\underset{\displaystyle (CH_2)_5CH_3}{\underset{|}{C}}HCH_2CH{=}CH(CH_2)_7COOH$$

Dimer (ricinoleo-ricinoleic acid)

3. *Pyrolysis.* Ricinoleic acid can be pyrolysed at temperatures above 275°C, yielding oenanthal and undec-10-enoic acid[9,10].

$$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOH \longrightarrow CH_3(CH_2)_5CHO + CH_2{=}CH(CH_2)_8COOH$$

Since the maximum temperature used in these experiments was 180°C, pyrolysis reactions were negligible.

The object of this work has been to determine the nature and extent of the reactions occurring in ricinoleic acid at elevated temperatures and at room temperature.

EXPERIMENTAL

Preparation of ricinoleic acid. Ricinoleic acid was separated from castor oil by the method of Hawke[3], which was modified to give a larger yield of acid of somewhat lower purity (see Table I).

Thermal treatment. Thermal treatment was carried out under nitrogen in 6 in. x 1 in. test tubes, which were immersed for the requisite periods in a constant temperature oil bath.

TABLE 1

Batch	Weight of Castor Oil (g)	Yield of Ricinoleic Acid (g)	Yield percentage of Theoretical*	Purity** per cent
Hawke	969	36·9	4·5	99·3
1	969	138·6	16·5	96·9
2	1162	300·1	30·2	98·4
3	533	118·9	25·6	96·6

*Assuming percentage of ricinoleic acid in castor oil=84[1].
**Based on hydroxyl value.

Analytical Constants. The following analytical constants were determined on each sample (each value reported is the mean of duplicate or replicate determinations):

1. Neutralisation value[3].
2. Hydroxyl value[3].
3. Saponification value. The standard method[11] was modified as follows:

Sample weight	:	0·5g
Normality of alcoholic potash	:	0·55
Volume of alcoholic potash	:	25 ml
Time of hydrolysis	:	2 h
Indicator	:	Thymolphthalein

4. Iodine value. The Wijs method[12] was used, employing 0·1 g samples, 20 ml Wijs solution and allowing 30 min for reaction time.
5. Total and conjugated diethenoid acids[13].

RESULTS

Samples of ricinoleic acid weighing approximately 15 g were thermally treated for varying periods at three temperatures, viz. 180°C, 147°C and 122·3°C. The results of analyses carried out on the products were based on one gram of the sample as analysed, with the exceptions of the mean molecular weight (M) and the percentage loss in weight (% loss). For calculation purposes it is necessary that the "analytical constants" of each batch have the same basis, and this has been chosen arbitrarily as one gram of the starting material for that batch. Changes in analytical constants are then a direct indication of the reactions of the active groups in one gram of starting material.

The analytical results (corrected for this change in weight) are reported in Table II, in which the following symbols have been used:

θ	:	Period of heat treatment (hours)
F	:	Correction factor for loss in weight
S	:	Saponification value (mg KOH/g)
$\overline{S}$	:	Arithmetic mean of S
A	:	Neutralisation value (mg KOH/g)
E	:	Ester value = $(\overline{S}-A)$(mgm KOH/g)
H	:	Hydroxyl value (mgm KOH/g)
C	:	(A—H) mg KOH/g
$\overline{C}$	:	Arithmetic mean of C
I	:	Iodine value (Wijs), (g I_2/100 g)
L	:	Total diethenoid acids (weight per cent)
L'	:	Conjugated diethenoid acids (weight per cent)
%Loss	:	Percentage loss in weight, as determined by direct weighing

The number mean molecular weights (M) are based on uncorrected neutralisation values, on the assumption that each molecule has one, and only one, carboxyl group. Values are presented graphically in Fig. 1.

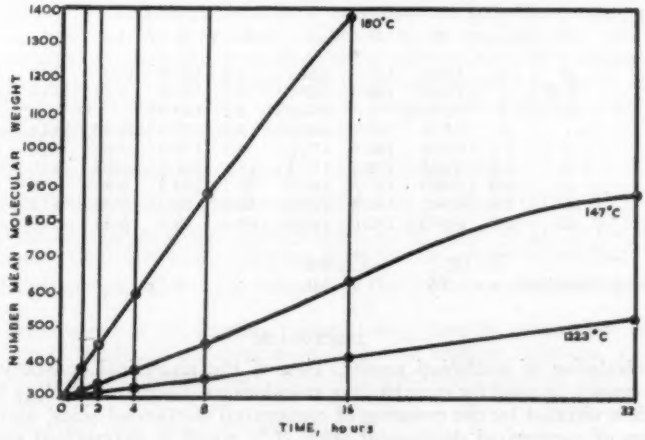

FIG. 1

TABLE II

Corrected analytical "Constants" after thermal treatment

Series 1 180°C

Sample No.	θ	% Loss	F	S	A	E	H	L	L′	I	C
1	0	0	1·000	188·0	187·7	0·6	181·3	0·44	0·08	86·0	6·4
2	0·25	0·4	0·995	187·9	174·0	14·3	171·5	0·57	0·10	84·5	2·5
3	0·5	0·8	0·988	190·3	164·0	24·3	160·2	0·41	0·09	84·3	3·8
4	1	1·4	0·980	188·0	147·1	41·2	143·5	0·47	0·09	84·5	3·6
5	2	—	0·9705	188·8	123·2	65·1	119·3	0·41	0·10	86·4	3·9
6	4	4·2	0·9595	187·8	90·8	97·5	88·5	0·62	0·12	84·1	2·3
7	8	4·9	0·951	188·1	61·5	126·8	58·2	0·69	0·14	83·1	3·3
8	16	6·3	0·943	187·5	38·3	150·0	34·9	0·62	0·23	85·4	3·4
				$\bar{S}=188·3$					$\bar{C}=3·7$		
Standard deviations:				$s=0·9$					$s=1·3$		

Series 2 147°C

Sample No.	θ	% Loss	F	S	A	E	H	L	L′	I	C
1	0	0	1·000	187·2	187·1	0	181·6	1·09	0·11	85·0	5·5
2	0·25	0·2	0·9995	187·1	184·3	2·7	180·8	1·14	0·10	85·0	3·6
3	0·5	0·1	0·9985	186·7	181·1	5·9	176·8	0·83	0·11	84·9	4·3
4	1	0·5	0·997	186·8	175·0	12·0	171·5	1·02	0·11	84·8	3·5
5	2	0·7	0·994	186·0	165·6	21·4	160·2	0·92	0·11	84·9	5·4
6	4	1·1	0·9885	187·5	150·0	37·0	143·6	0·79	0·10	83·8	6·4
7	8	2·3	0·9785	186·6	118·6	68·4	112·1	0·89	0·11	84·1	6·5
8	16	3·5	0·9645	187·3	86·2	100·8	82·9	0·95	0·11	84·3	3·3
9	32	4·5	0·9545	187·4	59·6	127·4	57·7	0·93	0·10	83·9	1·9
				$\bar{S}=187·0$					$\bar{C}=4·5$		
Standard deviations:				$s=0·5$					$s=1·6$		

Series 3 122·3°C

Sample No.	θ	% Loss	F	S	A	E	H	L	L′	I	C
1	0	0	1·000	187·0	185·5	1·7	180·8	0·93	0·11	86·3	4·7
2	0·25	0	1,000	186·6	185·1	2·1	180·8	0·83	0·10	86·9	4·3
3	0·5	0	0·9995	—	184·0	3·2	180·9	—	—	86·1	3·1
4	1	0	0·999	187·1	181·5	5·7	177·1	0·82	0·11	86·5	4·4
5	2	0·1	0·998	186·9	177·5	9·7	172·0	0·87	0·10	86·5	5·5
6	4	0·5	0·995	188·1	170·1	17·1	166·3	0·85	0·10	86·6	3·8
7	8	0·9	0·989	187·6	156·5	30·7	153·5	0·86	0·11	85·7	3·0
8	16	1·8	0·982	186·9	132·0	55·2	129·8	0·85	0·11	85·6	2·2
9	32	2·9	0·9705	187·0	102·4	84·8	99·3	0·84	0·10	84·5	3·1
				$\bar{S}=187·2$					$\bar{C}=3·8$		
Standard deviations:				$s=0·5$					$s=1·0$		

DISCUSSION

Interpretation of analytical results. Two of the analytical constants shown in Table II cannot be used for quantitative calculations. They are the Wijs iodine value (I), which is vitiated by the presence of conjugated diethenoid acids, and the weight percentage of conjugated diethenoid acids (L′), which is determined spectrophotometrically, assuming an extinction coefficient which may not be accurate, because

it has been assumed to be the same as that given by Hilditch *et al*[13] for linoleic acid which has been isomerised to the conjugated form by heating with an alkali. However, both these constants are useful qualitative indications of the reactions taking place during heat treatment. Reference to Table II shows the change of iodine value with time of heat treatment to be negligible while the quantities of conjugated diethenoid acids are insignificant at all times.

The neutralisation value (A) is a measure of the number of free carboxyl groups and is therefore reduced only by reactions which eliminate such groups, i.e. esterification.

The hydroxyl values are calculated by Hawke's formula[14]:

$$H = A - \frac{56{\cdot}1(V_h - V_b)N}{w}$$

$$\text{or } (A - H) = \frac{56{\cdot}1(V_h - V_b)N}{w} = C$$

where: V_h is the titre of the hydroxyl value determination
V_b is the titre of the blank determination
N is the normality of the alkali used for titrating
w is the weight of sample used.

The value of C is here subject to a considerable experimental error. The weight of sample is limited to 1·5 g[14], while the alkali must be 0·55N in order to keep the titre within the capacity of a 50 ml burette. The value of $\overline{C}$ is about 3·8 and, hence,

$$3{\cdot}8 = \frac{56{\cdot}1(V_h - V_b)0{\cdot}55}{1{\cdot}5}$$

$$(V_h - V_b) = 0{\cdot}18\text{ml}$$

It is obvious that a combined error of one drop (0·03 ml) in judging the two end-points will cause an error of 17 per cent in the value of C; this sensitivity is reflected in the wide variations of the values presented in Table II.

The value C is important because it indicates the reactions taking place. If it increases, it indicates the formation of linoleic acids and possibly pyrolysis. If it remains constant, then estolide formation is the sole reaction; if it decreases, it indicates the formation of new hydroxyl groups. It will be seen (in Table II) that the value of C remains approximately constant in these series of experiments, indicating the predominance of esterification reactions.

Composition of the starting materials. It is assumed that:

1. All saturated fatty acids are removed during purification[14].

2. The small amount of estolides in the starting material are in the form of the dimer (ricinoleo-ricinoleic acid), since condensation is a stepwise reaction[15].

3. A small amount of acetone remains in the acid after the purification process.

The constituents of the starting material may then be assumed to be ricinoleic acid, oleic acid, "linoleic" acids, ricinoleo-ricinoleic acid and acetone. The compositions of the starting materials may then be calculated from four of the analytical constants, viz.

The mean corrected saponification value ($\overline{S}$)

The mean value of C ($\overline{C}$)

The ester value of the starting material (E_1)

The weight percentage of diethenoid acids (L)

The compositions of the starting materials calculated from these data are reported n Table III.

TABLE III

Percentage composition of freshly prepared ricinoleic acid

Constituent	Series 1	Series 2	Series 3
Ricinoleic acid	97·5	97·1	95·7
Oleic acids	1·4	1·1	1·0
Linoleic acids	0·4	1·1	0·9
Ricinoleo-ricinoleic acid	0·6	0	1·8
Acetone	0·1	0·7	0·6
	100·0	100·0	100·0

Kinetics of estolide formation. Esterification is usually a second-order reaction, and it is assumed that this applies also to estolide formation. Bearing in mind that the neutralisation value (A) is a measure of the number of free carboxyl groups, the hydroxyl value (H) of the free hydroxyl groups, and the ester value (E) of the estolide linkages. the probable kinetic equation may be written:

$$\frac{dE}{d\theta} = k(A)(H)$$

where "k" is a velocity constant

Since $E=\overline{S}-A$ and $H=A-\overline{C}$

$$-\frac{dA}{(A)(A-\overline{C})} = kd\theta$$

which, on integration, yields the expression:

$$\theta = \frac{2{\cdot}303}{k\overline{C}} \text{ Log } \frac{A}{A-\overline{C}} + b \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where "b" is a constant of integration.

It follows that, if the reaction is of the second order as assumed, the curve of θ versus log $\frac{A}{A-\overline{C}}$ will be a straight line. Such curves are plotted in Fig. 2 and the values of the constants "b" and "k" are reported in Table IV.

TABLE IV

Velocity of estolide formation, values of constants

Series	Temperature	b	k
1	180°C	— 3·888	$14{\cdot}0 \times 10^{-4}$
2	147°C	—13·88	$3{\cdot}87 \times 10^{-4}$
3	122·3C	—38·88	$1{\cdot}40 \times 10^{-4}$

The effect of temperature on the rate of reaction. It was expected that the velocity constant would vary with temperature according to the Arrhenius equation:

$$\frac{d(\ln k)}{dT} = \frac{G}{RT^2}$$

where T is the absolute temperature (degrees Kelvin)
G is a constant related to the energy of activation
R is the gas constant.

Taking logarithms of the integrated form of this expression we obtain

$$\log k = \log \gamma - \frac{G}{RT} \log e$$

where γ=the integration constant or collision factor.

Thus it follows that the curve of log k versus $\frac{1}{T}$ should be a straight line (see Fig. 3).

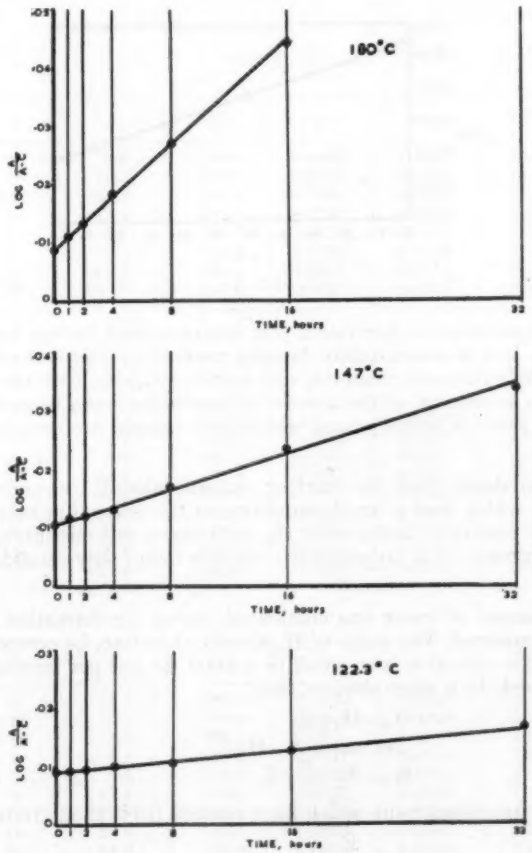

FIG. 2

The equation to this line (for 393°K<T<453°K) is:

$$\log k = 3{\cdot}94 - \frac{3080}{T} \quad .. \; .. \; .. \; .. \; .. \; .. \quad (2)$$

Molecular weight distribution of the estolides:

1. *The mean degree of polymerisation.* The formation of estolides is a linear polycondensation, with the elimination of (n−1) molecules of water for each chain of n units. Overbeek[16], using the method developed by Flory[17], has shown that for this type of reaction

$$\overline{DP}_n = \frac{p}{1-p} \quad .. \; .. \; .. \; .. \; .. \; .. \; .. \; .. \quad (3)$$

where $\overline{DP}_n$ is the mean degree of polymerisation
p is the fraction of functional pairs originally present which have reacted.

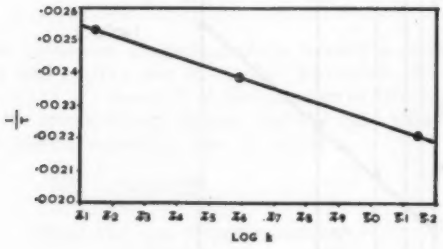

FIG. 3

In these experiments a functional pair is represented by one hydroxyl and one carboxyl group. If it is assumed that the only molecules present which have hydroxyl groups attached to them are ricinoleic acid and its estolides, then the hydroxyl value can be taken as a measure of the number of unreacted pairs at each time interval. The number of pairs of active groups which have reacted are measured by the ester value.

It has been shown that the starting material already contains some estolides (c.f. Table III), which bind a small proportion of the original pairs of active groups. It is therefore necessary to find a value H_0, such that it is a measure of the number of pairs of active groups in a (hypothetical) sample before any estolide formation has taken place.

A small amount of water was eliminated during the formation of the estolides in the starting material. The value of H_0 should, therefore, be corrected for this loss in weight, but the corection is so small (F=1·003 for one per cent of estolides) that it may be ignored. It is then obvious that:

$$H_0 = H_1 + E_1$$

and, since $A - H = \bar{C}$

$$H_0 = A_1 - \bar{C} + E_1 \quad .. \; .. \; .. \; .. \; .. \; .. \; .. \; .. \quad (4)$$

The fraction of functional pairs which have reacted (p) is then given by:

$$p = \frac{E}{H_0} \quad .. \; .. \; .. \; .. \; .. \; .. \; .. \; .. \; .. \quad (5)$$

The value of "p" can then be substituted in equation (3). The values of p, (1−p) and $\overline{DP}_n$ for each sample are reported in Table V.

It is noteworthy that molecules which have carboxyl but no hydroxyl groups (monofunctional) act as stabilisers and set a theoretical limit to the mean degree of polymerisation. Overbeek[16] has shown that:

$$\overline{DP}_{n(max)} = \frac{2+r}{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where $\overline{DP}_{n(max)}$ is the limiting value of the mean degree of polymerisation

r is the ratio of monofunctional to bifunctional molecules.

Since the number of bifunctional molecules is proportional to H_0, and since the number of monofunctional molecules is proportional to $\overline{C}$:

$$r = \frac{\overline{C}}{H_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

TABLE V

Series 1 180°C

Sample No.	θ	E	H_0	p	1–p	$\overline{DP}_n$	$\overline{M}'$
1	0	0·6	184·6	0·0033	0·9967	1·003	299·3
2	0·25	14·3	184·6	0·0775	0·9225	1·084	322·0
3	0·5	24·3	184·6	0·1316	0·8684	1·151	340·8
4	1	41·2	184·6	0·2284	0·7716	1·295	318·2
5	2	65·1	184·6	0·3527	0·6473	1·545	451·2
6	4	97·5	184·6	0·5282	0·4718	2·119	612·1
7	8	126·8	184·6	0·6869	0·3131	3·195	914·0
8	16	150·0	184·6	0·8127	0·1873	5·348	1517·0

Series 2 147°C

Sample No.	θ	E	H_0	p	1–p	$\overline{DP}_n$	$\overline{M}'$
1	0	0	182·6	0	1·0000	1·000	298·5
2	0·25	2·7	182·6	0·0148	0·9852	1·015	302·7
3	0·5	5·9	182·6	0·0323	0·9677	1·034	307·8
4	1	12·0	182·6	0·0657	0·9343	1·070	318·2
5	2	21·4	182·6	0·1171	0·8829	1·132	335·7
6	4	37·0	182·6	0·2026	0·7974	1·254	369·8
7	8	68·4	182·6	0·3746	0·6254	1·599	466·4
8	16	100·8	182·6	0·5520	0·4480	2·232	644·1
9	32	127·4	182·6	0·6997	0·3023	3·309	945·9

Series 3 122·3°C

Sample No.	θ	E	H_0	p	1–p	$\overline{DP}_n$	$\overline{M}'$
1	0	1·7	183·4	0·0093	0·9907	1·009	300·9
2	0·25	2·1	183·4	0·0115	0·9885	1·012	301·8
3	0·5	3·2	183·4	0·017	0·9825	1·018	303·4
4	1	5·7	183·4	0·0311	0·9689	1·032	307·4
5	2	9·7	183·4	0·0529	0·9471	1·056	314·1
6	4	17·1	183·4	0·0932	0·9068	1·103	327·3
7	8	30·7	183·4	0·1674	0·8326	1·200	354·5
8	16	55·2	183·4	0·3009	0·6991	1·431	419·3
9	32	84·8	183·4	0·4624	0·5376	1·859	539·3

The values of $\overline{DP}_{n(max)}$ for the three samples of material used are 101, 82, and 97. Comparison with Table V will show that the limiting values were not approached in these experiments.

2. *Molar distribution of polymers.* From the laws of probability, it may be shown[17] that:

$$P_n=p^{n-1}(1-p) \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (8)$$

where P_n is the molar fraction of polymers with degree of polymerisation "n"

p is the fraction of functional pairs, originally present, which have reacted.

By substituting the values of p and (1−p) at each time interval (see table V) in equation (8), and by putting n successively equal to 1, 2, 3, . . . etc., it is possible to calculate the molar fractions of monomers, dimers, trimers, etc. for each value of θ. The results are summarised in Tables VI, VII and VIII.

3. *Weight distribution of polymers.* The chemical formula for the estolides of ricinoleic acid may be written:

$$C_{18}H_{33}O_2\ [C_{18}H_{32}O_2]_{(n-2)}\ C_{18}H_{33}O_3$$

where "n" is the degree of polymerisation.

If the molecular weight of an estolide, degree of polymerisation "n", is denoted by M'_n, then

$$M'_n=281{\cdot}45+(n-2)280{\cdot}44+297{\cdot}45$$

$$\text{whence } M'_n=280{\cdot}44n+18{\cdot}02 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9)$$

Overbeek[16] made the simplifying assumption that the molecular weights of the polymers are simple multiples of one of the "internal" units of the chain.

This assumption is only justified when the degree of polymerisation is high and is by no means true for the present experiments, since the majority of estolides have degrees of polymerisation between one and ten. When n=1, the error incurred in the approximation is 6·4 per cent, and it was therefore necessary to derive a more accur--ate equation. This was done as follows:

The mean molecular weight of ricinoleic acid and its estolides can be calculated by substituting the mean degree of polymerisation for "n" in equation (9)

$$\overline{M'}=280{\cdot}44\ (\overline{DP}_n)+18{\cdot}02 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10)$$

where $\overline{M'}$ is the mean molecular weight of ricinoleic acid and its estolides.

The values of $\overline{M'}$ are listed in Table V.

The mean molecular weight of the estolides is also the sum of the molecular weights of the constituent polymers multiplied by their respective molar fractions, i.e.:

$$\overline{M'}=(P_1M'_1+P_2M'_2+P_3M'_3 \ldots .)$$

$$\overline{M'}=\sum_{n=1}^{n=\infty} P_nM'_n \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (11)$$

But, if W_n is the weight fraction of a polymer with degree of polymerisation "n", then:

$$W_n = \frac{\text{Weight of estolides with degree of polymerisation "n"}}{\text{Total weight of monomer + estolides}}$$

$$W_n = \frac{P_n M'_n}{\sum_{n=1}^{n=\infty} P_n M'_n}$$

and, substituting from equation (11)

$$W_n = \frac{P_n M'_n}{\overline{M'}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

The values of W_n for all samples are listed in Tables VI, VII and VIII.

4. *Weight percentage of a given polymer.* W_n is the weight fraction of a polymer (degree of polymerisation n) based on only the weight of ricinoleic acid and its estolides. It may be converted to weight percentage of an actual sample as follows: Consider one gram of starting material, heat treated for θ hours.

$$\text{Weight of ricinoleic acid+estolides} = \frac{(H)\,(\overline{M'})}{56{\cdot}1(1000)} \text{ grams}$$

where H is the corrected hydroxyl value

56·1 is the molecular weight of potassium hydroxide

$\overline{M'}$ is the mean molecular weight of ricinoleic acid and its estolides.

Therefore, the weight of an estolide with degree of polymerisation "n"

$$= \frac{(H)\,(\overline{M'})\,(W_n)}{56100} \text{ grams}$$

But, the weight of one gram of starting material after θ hours of heat treatment = F grams

where F is the factor to correct for loss in weight.

$$\text{Therefore, } (\%)_n = \frac{(H)\,(\overline{M'})\,(W_n)\,(100)}{56100\,F}$$

$$\text{or } (\%)_n = \frac{(H)\,(\overline{M'})\,(W_n)}{561\,F} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

where $(\%)_n$ is the weight percentage of estolide, degree of polymerisation "n", in a sample.

When using fairly pure material, as in these experiments, $(\%)_n$ is very nearly $100W_n$.

Reactions of ricinoleic acid at room temperature. A sample of ricinoleic acid was allowed to stand for six weeks in the dark in a loosely stoppered container. The temperature varied between 15°C and 20°C. The sample was analysed at the beginning and end of the period, and the corrected analytical constants are reported in Table IX. From these data the compositions of the starting material and of the products have been calculated and are presented in Table X.

Velocity constant of estolide formation. Assuming that estolide formation follows the normal second order kinetic equation. it may be calculated that

$$k = 0{\cdot}03 \times 10^{-4}$$

TABLE VI

Distribution of Polymers

Series 1 180°C

Sample No.		1		2		3		4		5		6		7		8	
θ (hours)		0		0·25		0·5		1		2		4		8		16	
	n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n
Monomer	1	0·997	0·994	0·923	0·855	0·869	0·761	0·772	0·604	0·647	0·428	0·472	0·230	0·313	0·102	0·187	0·037
Dimer	2	0·003	0·006	0·072	0·129	0·114	0·194	0·176	0·268	0·229	0·293	0·249	0·236	0·215	0·136	0·152	0·058
Trimer	3			0·005	0·015	0·015	0·038	0·040	0·091	0·081	0·153	0·132	0·185	0·148	0·139	0·124	0·070
Tetramer	4				0·001	0·002	0·007	0·009	0·027	0·028	0·072	0·070	0·129	0·101	0·127	0·101	0·076
Pentamer	5							0·002	0·008	0·010	0·032	0·037	0·085	0·070	0·108	0·082	0·077
Hexamer	6							0·001	0·002	0·004	0·013	0·019	0·054	0·048	0·089	0·066	0·075
Heptamer	7									0·001	0·005	0·010	0·033	0·033	0·071	0·054	0·070
Octamer	8										0·002	0·006	0·020	0·023	0·056	0·044	0·065
Nonamer	9										0·001	0·003	0·012	0·016	0·043	0·036	0·060
Decamer	10										0·001	0·002	0·007	0·011	0·033	0·029	0·054
Higher Polymers													0·009	0·022	0·096	0·125	0·358

TABLE VII

Distribution of Polymers

Series 2 147°C

Sample No.		1		2		3		4		5		6		7		8		9	
θ (hours)		0		0.25		0.5		1		2		4		8		16		32	
	n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n
Monomer	1	1·000	1·000	0·985	0·971	0·968	0·938	0·934	0·876	0·883	0·785	0·797	0·644	0·625	0·400	0·448	0·208	0·302	0·095
Dimer	2			0·015	0·028	0·031	0·059	0·062	0·112	0·104	0·178	0·162	0·253	0·234	0·291	0·247	0·222	0·211	0·129
Trimer	3				0·001	0·001	0·003	0·004	0·011	0·012	0·031	0·033	0·076	0·088	0·162	0·137	0·182	0·147	0·134
Tetramer	4								0·001	0·001	0·005	0·007	0·021	0·033	0·080	0·075	0·133	0·103	0·124
Pentamer	5										0·001	0·001	0·005	0·012	0·038	0·042	0·092	0·072	0·108
Hexamer	6												0·001	0·005	0·017	0·023	0·061	0·050	0·090
Heptamer	7													0·002	0·007	0·013	0·039	0·035	0·073
Octamer	8													0·001	0·003	0·007	0·025	0·024	0·058
Nonamer	9														0·001	0·004	0·015	0·017	0·046
Decamer	10														0·001	0·002	0·009	0·012	0·035
Higher Polymers																0·002	0·014	0·027	0·108

TABLE VIII

Distribution of Polymers

Series 3 122·7°C

Sample No.		1		2		3		4		5		6		7		8		9	
θ (hours)		0		0·25		0·5		1		2		4		8		16		32	
	n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n	P_n	W_n
Monomer	1	0·991	0·983	0·989	0·978	0·983	0·966	0·969	0·941	0·947	0·900	0·907	0·827	0·833	0·701	0·699	0·498	0·538	0·298
Dimer	2	0·009	0·017	0·011	0·022	0·017	0·033	0·030	0·057	0·050	0·092	0·084	0·084	0·139	0·228	0·210	0·291	0·249	0·267
Trimer	3						0 001	0·001	0·002	0·003	0·007	0·008	0·008	0·023	0·056	0·063	0·130	0·115	0·183
Tetramer	4										0·001	0·001	0·003	0·004	0·013	0·019	0·052	0·053	0·112
Pentamer	5													0·001	0·002	0·006	0·019	0·025	0·065
Hexamer	6															0·002	0·007	0·011	0·036
Heptamer	7																0·002	0·005	0·019
Octamer	8																0·001	0·003	0·010
Nonamer	9																	0·001	0·004
Decamer	10																		0·003
Higher Polymers																			0·003

TABLE IX

Corrected analytical constants of ricinoleic acid after standing at room temperature

	F	S	A	H	I	L	L′	E	C
Freshly prepared ricinoleic acid	1·000	187·0	185·5	180·8	86·8	0·93	0·11	1·5	4·7
After 6 weeks at room temperature	0·972	187·0	122·7	119·6	84·1	0·38	0·10	64·3	3·1

TABLE X

Percentage composition of ricinoleic acid after standing at room temperature

Constituent	Starting material	After 6 weeks at room remperature
Ricinoleic acid	95·4	41·7
Estolides: Dimer	1·5	28·6
Trimer	0	15·0
Tetramer	0	6·7
Pentamer	0	3·1
Hexamer	0	1·6
Heptamer	0	0·5
Octamer	0	0·2
Nonamer	0	0·1
Oleic Acid	1·4	1·4
Linoleic acids	0·9	0·4
"Dihydroxy octadecenoic acid"	0	0·6
Acetone	0·8	0

CONCLUSION

When ricinoleic acid is heated in an inert atmosphere, the main reaction is the formation of estolides, this reaction being of the second order. The molecular weight distribution of the products can be calculated from the laws of polycondensation.

When ricinoleic acid is allowed to stand at room temperature, the main reaction is again estolide formation.

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THE AUTO-REACTIONS OF RICINOLEIC ACID
PART II. CATALYSED DEHYDRATION OF RICINOLEIC ACID

by

F. HAWKE and E. A. KOHLL

OPSOMMING

As risinoleïesuur chemies ontwater word by 'n temperatuur van 180°C in the aanwesigheid van natrium bisulfaat vind die reaksie plaas in twee stadia. Gedurende die eerste stadium word kortketting-estoliede en diëtileensure gevorm, saam met klein hoeveelhede enantol en undek-9-eensuur. Wanneer die hidroksiewaarde die nulpunt nader begin die estoliedkettings te breek, weereens met die formasie van diëtileensure. Dit skyn asof die laasgenoemde reaksie hoofsaaklik die gekonjugeerde oktadeka-9:11-diensuur produseer.

Estoliedformasie skyn 'n tweede-orde reaksie te wees met betrekking tot neutralisasie- en hidroksielwaardes, en chemiese ontwatering eerste orde met betrekking tot hidroksielwaarde. 'n Vergelyking word afgelei wat die neutralisasiewaarde in verband bring met die gewigspersent diëtileensure gevorm gedurende die eerste stadium van die reaksie.

SUMMARY

When ricinoleic acid is chemically dehydrated at 180°C in the presence of sodium bisulphate, the reaction proceeds in two stages. In the first stage, short-chain estolides and diethenoid acids are formed, together with some oenanthal and undec-10-enoic acid. As the hydroxyl value approaches zero, rupture of the estolide chains commences, with the formation of further quantities of diethenoid acids. It appears that the latter reaction results mainly in the formation of the conjugated octadeca-9:11-dienoic acid.

Estolide formation appears to be a second-order reaction with respect to neutralisation and hydroxyl values, and chemical dehydration first order with respect to hydroxyl value. An equation has been derived relating the neutralisation value to the weight percentage of diethenoid acids formed during the first stage of the reaction.

INTRODUCTION

In a previous paper[1] it was pointed out that the main reaction taking place in ricinoleic acid at temperatures up to 180°C and in the absence of a catalyst, was the formation of estolides. This paper is concerned with the reactions taking place when ricinoleic acid is heat-treated at 180°C in the presence of five per cent of anhydrous sodium bisulphate.

The catalysed dehydration of castor oil fatty acids is a process of industrial importance, as it forms a step in the production of dehydrated castor oil by the Scheiber process[2, 3, 4, 5]. It was hoped that the present work would provide information about the products from this type of dehydration.

EXPERIMENTAL

Ricinoleic acid was separated from castor oil fatty acids by low-temperature crystallisation from acetone[6]. Approximately fifteen-gram samples were heat treated at 180°C in 6 in. x 1 in. test tubes in the presence of five per cent anhydrous sodium bisulphate under an atmosphere of dry nitrogen. The test tubes were withdrawn from the constant temperature bath at definite intervals and the samples were filtered immediately under vacuum. The filtrates were cooled rapidly and analysed. Analytical constants were determined as described previously[1].

RESULTS

The analytical results (corrected for change in weight during heat treatment) are reported in Table 1. The symbols used are described in Part 1, p. 3.

DISCUSSION

Estolide Chains. It will be seen (Table 1) that the hydroxyl value drops to zero after eight hours. This means that all the hydroxyl groups, including those normally present at the end of each estolide chain, are removed during the treatment. The estolide chains are then incapable of further condensation, since the loss of the terminal hydroxyl groups has the same effect as the presence of monofunctional stabilisers, i.e. it limits the maximum mean degree of polymerisation. Therefore, the estolide chains formed in the presence of a catalyst are comparatively short.

Formation of linoleic acids and rupture of estolide chains. The most striking difference between the compositions of samples, heat treated in the absence and presence of a catalyst, lies in the systematic rise in weight percentage of diethenoid acids resulting from the latter treatment. This is also reflected in increasing values of C and, to a limited extent, in the iodine values.

The change in the weight percentage of total and conjugated diethenoid acids with time are represented graphically in Fig. 1. It will be seen that the curves of L and L′ are roughly similar, which suggests that the ratio L′:L may be a constant. This ratio is reported in Table 1. It will be seen that the ratio does remain approximately constant for the first two hours, but thereafter the proportion of conjugated acid increases. This fact is interesting because it appears to correspond to the commencement of a new reaction, i.e. the rupture of estolide chains.

TABLE I

Corrected analytical "constants" after thermal treatment

Sample No.	θ	F	S	A	E	H	C	I*	L	L′	L′/L
1	0	1·000	188·9	186·1	2·8	181·6	4·5	86·1	0·87	0·04	—
2	0·25	0·972	188·4	130·3	58·6	110·1	20·2	88·8	7·23	3·44	0·476
3	0·5	0·961	189·0	89·7	99·2	57·0	32·7	88·7	12·88	5·69	0·441
4	1	0·948	188·8	64·9	124·0	25·6	39·3	88·5	16·36	8·00	0·489
5	2	0·938	188·9	53·8	135·1	7·8	45·0	89·0	18·49	8·75	0·473
6	4	0·935	188·6	49·7	139·2	2·0	47·7	92·3	18·97	10·09	0·531
7	8	0·931	189·0	53·2	135·7	0	53·2	90·6	22·48	12·40	0·551

$\bar{S}$=188·9
Standard deviation: s= 0·4

* The Wijs Iodine values were extremely variable, due to the presence of large quantities of conjugated diethenoid acids.

Evidence for this reaction is summarised below:

1. The number mean molecular weight and the ester value both rise to a maximum and then decrease (see Table 1 and Fig. 2). This indicates rupture of the estolide chains at the ester bonds.

2. The curves of percentage diethenoid acid versus period of heating (Fig. 1) have points of inflexion at $\theta \sim 3$ to 4 hours. This indicates the commencement of a new reaction.

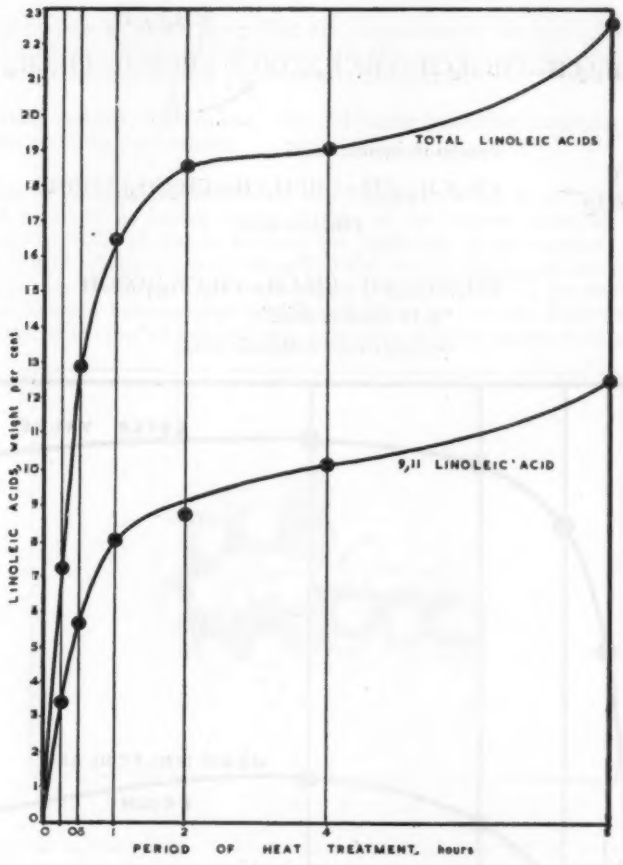
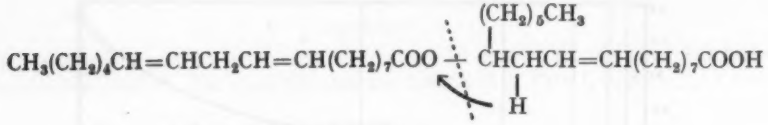


FIG. 1

3. These curves (Fig. 1) show no sign of reaching a maximum after eight hours, despite the fact that the hydroxyl value has dropped to zero at this stage. This shows that besides the normal chemical dehydration there is another reaction which produces linoleic acids.

4. The neutralisation value reaches a minimum after four hours, and thereafter increases (Table 1). This indicates the freeing of carboxyl groups formerly bound in estolide linkages.

From the foregoing evidence it appears that, after about three hours of heat treatment, rupture of estolide chains, previously terminated by elimination of the terminal hydroxyl group, commences, with the formation of linoleic acids. The equation for the dimer is given below:



linoleo-ricinoleic acid

$\xrightarrow[(NaHSO_4)]{180°C}$ $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$

Linoleic acid

+

$CH_3(CH_2)_5CH=CH.CH=CH(CH_2)_7COOH$

"9,11 linoleic acid"

(octadeca-9:11-dienoic acid)

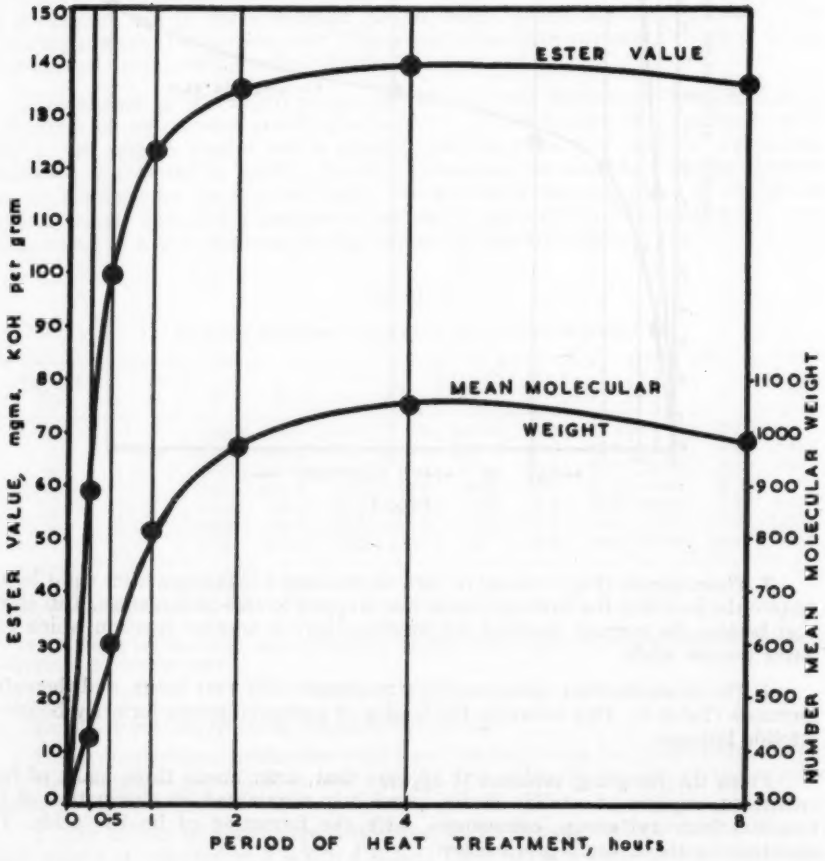


FIG. 2

It will be noted, furthermore, that the proportion of conjugated acid begins to rise after four hours (Table 1), which indicates that estolide rupture provides a higher proportion of conjugated acids than normal dehydration.

Suggested reaction mechanisms. The following tentative suggestions are made for possible reaction mechanisms.

1. *Simple chemical dehydration.* It is assumed that the ricinoleic acid molecule curls back on itself, as shown in Fig. 3. One of the oxygen atoms of the carboxyl group is then ideally placed to activate the hydrogen atoms on number 13 carbon atom, but it is too distant to activate any of the other hydrogen atoms. The hydrogen atoms on number 11 carbon atom receive only a slight activation, due to the proximity of the double bond between numbers 9 and 10 carbon atoms. Therefore, the main product from this type of dehydration is linoleic acid (octadeca-9:12-dienoic acid).

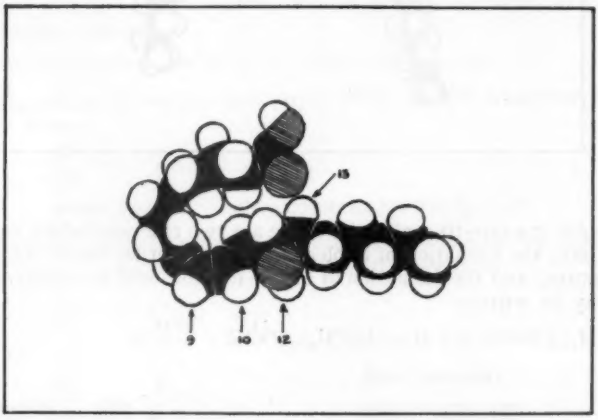


FIG. 3

2. *Estolide rupture.* Fig. 4 illustrates a possible structure of a typical simple condensation product (linoleo-ricinoleic acid). It will be seen that in addition to electromeric activation due to the neighbouring ester linkage on number 12 carbon atom, the hydrogen atoms on the 11th and 13th carbon atoms are equally activated by the close proximity of one of the oxygen atoms of the ester group. Since the hydrogen atoms on the 11th carbon atom are further activated by the neighbouring double bond, between numbers 9 and 10, it may be expected that the conjugated 9, 11 linoleic acid will form a greater proportion of the reaction product.

The Scheiber process[2, 3, 4] for the production of dehydrated castor oil involves the heat treatment of castor oil fatty acids in the presence of a catalyst. In the light of the above evidence the following reactions can be postulated for this process:

1. Dehydration, producing a mixture of diethenoid acids and comparatively short-chain estolides. Linoleic acid will predominate in the diethenoid acids formed during this stage of the reaction.

2. Rupture of estolides, producing further quantities of diethenoid acids, of which 9,11 linoleic acid forms the major component.

This mechanism supports Scheiber's claims[6] that the product from his process contains a higher proportion of conjugated acids than that obtained by directly dehydrating castor oil.

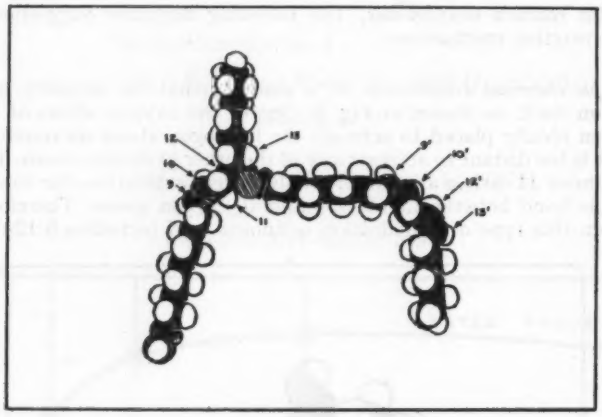


FIG. 4

Formation of undec-10-enoic acid. There are two reactions which can increase the value of C, *viz.*, the formation of linoleic acids (whether by direct dehydration or by estolide rupture), and the formation of undec-10-enoic acid by pyrolysis[7]. The latter reaction may be written

$$\underset{\text{ricinoleic acid}}{CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOH} \xrightarrow{\text{heat}}$$

$$\underset{\text{oenanthal}}{CH_3(CH_2)_5CHO} + \underset{\text{undec-10-enoic acid}}{CH_2{=}CH(CH_2)_8COOH}$$

The "fractional value" of C due to linoleic acids may be calculated from

$$C_{Lin} = \frac{200{\cdot}1(L)}{100} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (i)$$

which, for Sample 1 (starting material) gives:

$$C_{Lin} = \frac{200{\cdot}1(0{\cdot}87)}{100} = 1{\cdot}7 \text{ mg KOH per g.}$$

Since there is no undecenoic acid present in the starting material, the other non-hydroxy acids (chiefly oleic acid) must account for the rest of C in Sample 1, i.e.,

$$C_{Oleic} = 4{\cdot}5 - 1{\cdot}7 = 2{\cdot}8 \text{ mg KOH per g.}$$

If it is assumed that C_{Oleic} remains constant throughout the treatment, the contribution of C_{Lin} may be calculated for each sample and hence the contribution of undec-10-enoic acid to the value of C may be found. It is then possible to calculate the weight per cent of undec-10-enoic acid in each sample. These figures are presented in Table II from which it can be seen that oenanthal formation is negligible.

TABLE II

Weight per cent undec-10-enoic acid in heat treated samples

Sample No.	θ	C	C_{Lin}	C_{Oleic}	$C_{Un.}$	Percentage undecenoic acid
1	0	4·5	1·7	2·8	0	0
2	0·25	20·2	14·5	2·8	2·9	1·0
3	0·5	32·7	25·8	2·8	4·1	1·3
4	1	39·3	32·7	2·8	3·8	1·2
5	2	45·0	37·0	2·8	5·2	1·7
6	4	47·7	38·0	2·8	6·9	2·3
7	8	53·2	45·0	2·8	5·4	1·8

Kinetics of condensation and dehydration. The following are the two main reactions occurring during the first stages of heat treatment in the presence of a catalyst.

1. Estolide formation.
2. Formation of linoleic acids by direct dehydration.

If it is assumed, as in our previous paper[1], that estolide formation is a second-order reaction, then:

$$\frac{dE}{d\theta} = k(A)(H) \qquad \text{(ii)}$$

where k is the velocity constant for the reaction.

It seems probable that the rate of formation of linoleic acids by direct dehydration is proportional to the concentration of hydroxyl groups, i.e.,

$$\frac{dL}{d\theta} = k''(H) \qquad \text{(iii)}$$

Dividing (ii) by (iii),

$$\frac{dE}{dL} = \frac{k}{k''}(A)$$

$$\text{or} \quad \frac{dE}{dL} = k'(A) \quad \text{where } k' = \frac{k}{k''}$$

$$\text{but} \quad E = \bar{S} - A$$

$$\text{therefore} \quad \frac{d(\bar{S}-A)}{dL} = k'(A)$$

$$\text{or} \quad -\frac{dA}{A} = k'.dL$$

Integrating and re-arranging

$$L = -\frac{2{\cdot}303}{k'} \log A + B \qquad \text{(iv)}$$

where B is a constant.

L is plotted against log A in Fig. 5; it will be seen that the curve approximates fairly well to a straight line except during the last stages of the treatment (i.e. Point 7, corresponding to a time of heating of 8 hours). The correlation coefficient for points 1 to 6 is r=0·9937. Omitting point 7, equation (iv) becomes:

$$L = 72{\cdot}70 - 31{\cdot}21 \text{ Log A (for } 0 < \theta < 4)$$

The analytical and calculated values for total linoleic acids are compared in Table III.

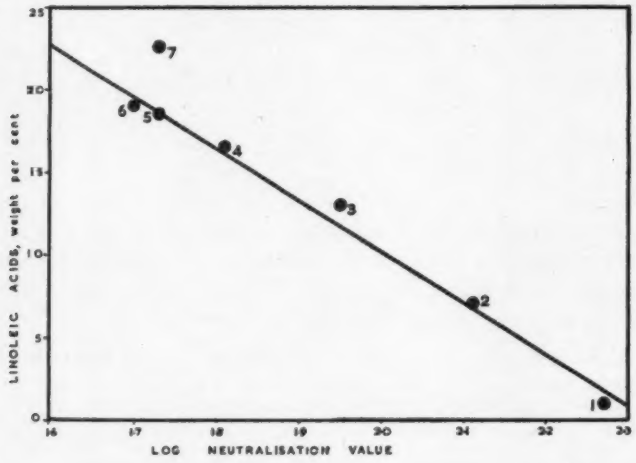


FIG. 5

TABLE III

Sample No.	θ	L	$L_{calc.}$
1	0	0·87	1·85
2	0·25	7·23	6·69
3	0·5	12·88	11·75
4	1	16·36	16·15
5	2	18·49	18·68
6	4	18·97	19·77
7	8	22·48	18·83

CONCLUSION

When ricinoleic acid is chemically dehydrated in the presence of sodium bisulphate, the reaction proceeds in two stages. In the first stage, short-chain estolides and diethenoid acids are formed, together with some oenanthal and undec-10-enoic acid. As the hydroxyl value approaches zero, rupture of estolide chains commences, with the formation of further quantities of diethenoid acids. It appears that the latter reaction results mainly in the formation of the conjugated octadeca-9:11-dienoic acid.

Estolide formation is a second-order reaction with respect to neutralisation and hydroxyl values, while chemical dehydration is first-order with respect to hydroxyl value.

The work reported was carried out in the Laboratories of the Department of Chemistry and Chemical Engineering, University of the Witwatersrand, and the

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Research Department,
African Explosives and Chemical Industries, Ltd.,
P.O. Northrand,
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AN ANALYTICAL METHOD FOR THE QUANTITATIVE DETERMINATION OF THE PRINCIPAL BIOLOGICALLY ACTIVE CONSTITUENT IN DELNAV, AN ORGANO-PHOSPHORUS INSECTICIDE

by

P. CASAPIERI and H. H. KEPPLER

OPSOMMING

Met behulp van inversfase-papierverdelingschromatografie is DELNAV, 'n organo-fosfortipe insektemiddel, in tenminste drie bestanddele geskei. Die hoofbestanddeel, 2, 3-p-dioksaanditiol S,S-bis (0, 0-dietiel fosforditioaat), ook D3P genoem, is herwin deur uitloging van die papier en die fosforinhoud is spektrofotometries bepaal.

SUMMARY

Using a reverse phase paper partition chromatographic technique, it is possible to resolve DELNAV, an organo-phosphorus insecticide, into at least three constituents. The principal constituent, 2, 3-p-dioxanedithiol S,S-bis (0,0-diethyl phosphorodithioate), D3P, is recovered from the paper by elution, and the phosphorus content determined spectrophotometrically.

INTRODUCTION

Delnav, also known as Hercules 528, and synthesised by Diveley *et. al.*,[1] is reputed to have excellent insecticidal and acaricidal activity. The principal biologically active constituent in the technical material is 2,3-p-dioxanedithiol S,S-bis (0,0-diethyl phosphorodithioate). This compound, which is now referred to as D3P, exists in both *cis* and *trans* forms. Diveley *et. al.*, have shown that 2-p-dioxenethiol S,S-bis- (0,0 diethyl phosphorodithioate) is a minor constituent of *Delnav*, as are also the closely related esters, 0,0,0-triethyl phosphorothioate and 0,0,S-triethyl phosphorodithioate. Because of the closely allied nature of these compounds, the need arose for an analytical method which would be specific for D3P in *Delnav*, and in spraywashes containing this mixture. Dunn[2] has developed a method which involves cleavage of the carbon sulphur bond of D3P when *Delnav* is treated with mercuric chloride. The resultant products, after hydrolysis, are glyoxal and ethylene glycol. The former is converted to the 2,4-dinitrophenylosazone, which on being made basic, gives an intense blue colour that may be measured spectrophotometrically. The method is, however, a lengthy one and in addition other glyoxal precursors in *Delnav* as well as contaminants of the osazone have to be removed.

We set out, therefore, to devise a procedure for the complete separation of D3P from either: (a) spraywashes containing *Delnav* or (b) *Delnav*. The procedure depends in the case of (a) on extraction of *Delnav* and in (a)and (b) on the chromatographic separation of D3P from the concentrated *Delnav* and its assay by determination of total phosphorus.

EXPERIMENTAL

(a) *Extraction of Delnav from spraywashes.* Aluminium sulphate (1g) was added to 50 ml. of a spraywash (nominally 0·1% *Delnav*) to break the emulsion. The mixture was extracted three times with 25 ml hexane aliquots. The combined hexane

solutions were concentrated to 2-3 ml, transferred to a 10 ml volumetric flask, and diluted with hexane to volume.

(b) *Delnav. Delnav* (0·5g) was diluted with hexane to exactly 100 ml.

(c) *Reverse phase paper partition chromatography.*

Apparatus: Whatman's No. 2 filter paper sheets (27·5 cm square) impregnated with medicinal paraffin from a 5% solution of medicinal paraffin in hexane. Conventional paper chromatographic apparatus for ascending chromatography. The supporting frame should be capable of carrying from 5-6 papers.

Reagents: The developing solvent (Kritchevsky and Tiselius[3]) consists of the upper phase of a mixture of $CHCl_3$, EtOH, H_2O/10,10,6, which should be equilibrated at the temperature used for chromatography. 0·2M mercuric chloride. 0·08M 2,4-dinitrophenylhydrazine in 32% $HClO_4$. 0·5% solution of 2,6-dibromo-N-chloro-p-quinoneimine in benzene (Meun *et. al.*[4]).

(i) *Resolution and identification of the constituents of Delnav.* Two chromatographic papers (A and B) were each separately "spotted" with *Delnav* and the reputed constituents of *Delnav.* The chromatograms were developed at constant temperature for 12 h, the papers removed from the tank and dried in a clean atmosphere. Paper (A) was sprayed with the quinoneimine reagent, then heated in an oven at 105°C for 10 min. Paper (B) was sprayed with mercuric chloride followed immediately with 2,4-dinitrophenylhydrazine. No heat treatment of this sprayed paper was required.

Paper (A).

The following three compounds were resolved from the *Delnav*:—

(i) 2,3-p-dioxanedithiol S,S-bis (0,0-diethyl phosphorodithioate) (D3P), yellow brown area, R_F 0·05.

(ii) 2-p-dioxenethiol-S-(0,0-diethyl phosphorodithioate), dark red area, R_F 0·4.

(iii) light pink area, R_F 0.90, due to a mixture of the closely related triethyl esters.

Paper (B).

Apart from D3P no other reference compounds developed a colour. The D3P was observed as a yellow area, R_F 0·05.

(ii) *Separation and quantitative recovery of D3P from Delnav.* A horizontal line was drawn in pencil 1 in. from the base of each of five papers. 0·2 Ml of the hexane solution containing the *Delnav* under examination was applied, using a micrometer syringe, uniformly along each line. The papers were developed as previously and dried. One paper was sprayed with the mercuric chloride solution followed by the 2,4-dinitrophenylhydrazine solution. Using this sprayed paper as a guide, strips containing the D3P were cut from the remaining unsprayed papers. The D3P was extracted separately from each strip with methanol (20 ml) for two hours in a Soxhlet apparatus of 15 ml capacity. After evaporation of solvent the phosphorus content of the residual mixture of D3P and liquid paraffin was determined.

(iii) *Phosphorous determination by the vanado-molybdate method*[5].

Reagents: Perchloric acid, 70-72%. Ammonium molybdate solution, 5%. Ammonium vanadate solution, 0·25% containing 150 ml $HClO_4$. Mixed reagent solution: mix equal volumes of ammonium molybdate and vanadate solutions; this solution must be prepared daily.

Perchloric acid (4 ml) was added to each flask containing the D3P and liquid paraffin. The solutions were boiled gently until a clear, colourless (or very pale yellow) solution resulted (1-3h). The contents of each flask were transferred with water (30 ml) to 50 ml volumetric flasks, mixed reagent (10 ml) was added and the solutions diluted to volume. To ensure that full colour development took place the solutions were allowed to stand for 60 min. The optical density of each solution was then measured against the reagent blank at 380 mμ in 1 cm cells using a spectrophotometer, Zeiss model PMQ II. The phosphorus content of each sample was interpolated from a calibration curve, prepared by treating various aliquots of standard phosphate solution (containing 40-400 μg P) with perchloric acid followed by the above procedure.

RESULTS

Because an empirical spectrophotometric method involving a calibration step is used, the phosphate determination can be considered to be free from bias. A synthetic sample of D3P, analysed by the above chromatographic procedure, was found to be 94% pure ($\pm$ 3% on fourteen determinations). Determination of the phosphorus content of unchromatographed D3P, assuming that all the phosphorus was present as D3P, gave a value of 103% ($\pm$ 1·5% on nine determinations). Evidently impurities, probably thioesters, with a higher phosphorus content were present; they would be resolved on chromatography and not be included in the D3P recovered. As no purer sample of D3P was available it is assumed that the recovery of D3P is sufficiently quantitative for the chromatographic method to have practical application.

The D3P content of *Delnav* was found to be 75% ($\pm$ 4% on fifteen determinations) and that of *Spraywash* (nominal concentration of *Delnav* 0·1%) 0·071%.

Since the D3P content of *Delnav* was found to be 75%, this factor was used in converting the D3P content of the spraywash to a *Delnav* content. This yielded 0·095% ($\pm$ 0·007%) which is in fair agreement with the nominal 0·1% *Delnav* concentration of the spraywash emulsion.

DISCUSSION

The perchloric acid concentration has a considerable effect on the colour developed by the phospho-vanado-molybdate complex. However, a reproducible optical density for a given phosphate concentration can be obtained when the concentration of perchloric acid in the final solution lies in the range 0·2 to 1·4 M. The presence of sulphates, in amounts as little as 20 p.p.m., tend to retard, but do not inhibit, colour formation. For this reason a time of one hour was allowed for complete colour development to take place.

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Research Department,
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WATER VAPOUR PRESSURE-TEMPERATURE RELATIONSHIPS FOR SATURATED AQUEOUS SOLUTIONS OF UREA

by

K. L. PIGGOTT

OPSOMMING

Die waterdampdruk oor versadigde oplossings van ureum in water is tussen 10°C en 80°C gemeet. Die waardes verkry pas, oor die hele temperatuurbestek wat ondersoek is, 'n vergelyking van die tipe voorgestel deur Rankine.

Wisseling van die biuret inhoud van die ureum tot en met 6·5% het weinig invloed op die waterdampdruk gehad. Die enigste betekenisvolle verskil was tussen die laagste biuret konsentrasie gebruik (0·3%) en die hoogste (6·5%), en dit het minder as 5 mm Hg bedra selfs by die hoogste temperature.

SUMMARY

The water vapour pressure has been measured over saturated aqueous solutions of urea from 10°C to 80°C. The values obtained were found to fit an equation of the form proposed by Rankine for the entire temperature range studied.

Variation in the biuret content of the urea up to 6·5 per cent was found to have little effect on the water vapour pressure. The only significant difference found was between the lowest biuret concentration used (0·3%) and the highest (6·5%) and this amounted to less than 5 mm Hg even at the highest temperatures.

INTRODUCTION

The water vapour pressure over saturated solutions of urea has been determined by a number of workers, but most of these measurements have been confined to the temperature range 10°C to 30°C[1, 2, 3]; only a few values are recorded for temperatures between 30°C and 80°C[4, 5, 6].

Perman and Lovett[5] considered solutions from low concentrations up to supersaturation at temperatures from 40°C to 80°C. A static method was used by these authors and they commented on the inaccuracy of the results obtained by one of them[7] for dilute solutions of urea using a dynamic method. In this earlier work, however, superiority was claimed for the dynamic method over the static method. In fact the two sets of vapour pressure data show reasonable agreement with each other.

In previous determinations of the water vapour pressure over saturated solutions of urea, the possible influence of biuret impurity has been neglected. The commercial material sometimes contains up to about 5% biuret so that measurements were made on samples of material prepared with biuret contents up to about this level. It might have been assumed that the effect of a comparatively low concentration of this impurity would have been insignificant in vapour pressure determinations. Indeed, when considered simply on the basis of the ideal solution laws it is found that this is the case. However, although urea has been considered as an ideal solute[3, 8, 9], even up to concentrations encountered in saturated solutions, interest has been limited to temperature ranges up to about 25°C. At the higher temperatures employed in the

present study, isomerization of urea and its subsequent decomposition[10,11,12], together with possible association between biuret and urea in solution[13] may imply non-ideal behaviour.

By selecting the temperatures from 10°C to 80°C this wide range would provide values useful in selecting a law to relate the temperature dependence of the vapour pressure. Sakai[6] has reported the results of his measurements between 18°C and 50°C in the form of two empirical equations of the type $\ln p = \frac{A}{T} + B$ covering the temperature ranges (a) 18°C to 30°C and (b) 20°C to 50°C. Values calculated for the second temperature range differ considerably from his experimental data which are in reasonable agreement with other published figures.

EXPERIMENTAL

The literature on the subject of vapour pressure measurement is extensive and the early work has been reviewed by Pearce and Snow[14] who classified and commented on the relative merits of the principal methods. More recently the general problem of vapour pressure determinations for organic compounds has been discussed[15]. Of those reported, the transpiration method has been extensively used. The chief criticism of the method has been the necessity to measure accurately the large quantity of gas transpired through the apparatus. Although the method of Pearce and Snow[14] fulfilled this requirement it is possible to avoid it altogether. The apparatus used in the present work was based on that of Bechtold and Newton[16] in which the gas was passed successively through saturators containing the solvent (pure water) and the solution under investigation (saturated solutions of urea), with absorption tubes after each set of saturators. Thus it was possible to eliminate the necessity for accurate gas volume measurement since the solution vapour pressure was simply expressed in terms of the water vapour pressure, the total pressure and the gain in weight of each absorber. This principle was in fact employed by Washburn and Heuse[17] in their work published some twenty-five years before that of Bechtold and Newton. A general arrangement of the apparatus finally used is given in Fig. 1.

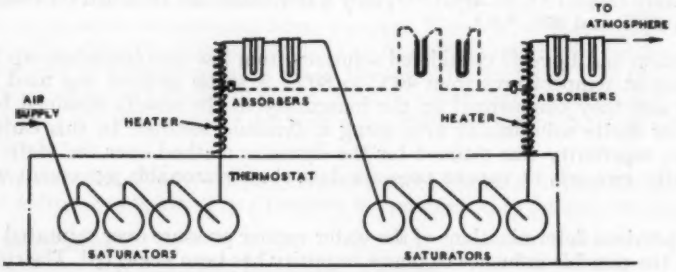

FIG. 1

General arrangement of apparatus

Considerable modification of the Bichowsky and Storch saturators[18] was found necessary to suit the conditions encountered with saturated solutions of urea. In particular it was found that the location of the bubble jet in the contact tube and the angle of inclination of the contact tube were critical for stable operation.

The water vapour pressure over the saturated solution was calculated by means of the following equation:

$$p_2 = \frac{p_1 \cdot m_2 \cdot P_2}{m_2 p_1 + m_1 (P_1 - p_1)} \text{ mm Hg} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where p=aqueous vapour pressure
P=total pressure at saturator outlet
m=gain in weight of absorber.

The subscripts 1 and 2 refer to the water and the saturated solution systems respectively.

Values for the vapour pressure of water were taken from the Physicalisch-technische Reichanstalt "Warmetabellen"[19].

Standard solutions of urea with different biuret contents were prepared from:

(a) a commercial product in the form of prills (biuret content 0·27%)
(b) Analar grade urea (biuret content 1·04%)
(c) a mixture of (b) and biuret, to give a product with a biuret content of 6·45%.

Since the operation of a large water-filled thermostat at high temperature represents considerable difficulty, it was decided to carry out the experiments in two groups:

(a) for the temperature range 10°C to 60°C
(b) for the temperatures of 70°C and 80°C.

The first temperature range (a) was treated as a factorial experiment for the variables of biuret content and temperature and the vapour pressure measurements of the various combinations were made in random order. For each of the temperatures in the second group (b), determinations were made at the three biuret levels.

Determination of urea decomposition: Since it is known[3,11] that in aqueous solutions urea decomposes to yield ammonia and carbon dioxide, experiments were carried out to estimate the extent to which it decomposed during the course of the vapour pressure measurements. For this purpose air was passed through initially saturated aqueous solutions of urea at the normal rate used in the vapour pressure measurements and at temperatures between 40°C and 80°C. The ammonia concentration of the effluent air stream was determined by the boric acid method over fifteen minute periods commencing at time intervals of one, two, four and six hours from the start of the experiments.

DISCUSSION

A number of vapour pressure equations have been recently reviewed by Cornelissen and Waterman[20] who have shown that those proposed by Nernst[21] and by Rankine[22] are both really expansions of the Clapeyron equation and should be more exact than the integrated form of the Clausius-Clapeyron relationship with the usual approximations.

The results of the present work were fitted to the Nernst, Rankine and integrated form of the Clausius-Clapeyron equations by using the mean values of the vapour pressures for each combination of temperature and biuret level. Although tests for closeness of fit are insensitive, since only mean values were used, it was found that those equations derived from the Rankine equation fitted the experimental data best.

The four regression equations derived are as follows, where 283°K<T<353°K:

0·3% biuret,

$$\ln p = 182{\cdot}236 - \frac{12062}{T} - 24{\cdot}374 \ln T \quad .. \quad .. \quad .. \quad .. \quad (2)$$

1·0% biuret,

$$\ln p = 172{\cdot}536 - \frac{11716}{T} - 22{\cdot}878 \ln T \quad .. \quad .. \quad .. \quad .. \quad (3)$$

6·5% biuret,

$$\ln p = 190{\cdot}313 - \frac{12371}{T} - 25{\cdot}601 \ln T \quad .. \quad .. \quad .. \quad .. \quad (4)$$

Average,

$$\ln p - 170{\cdot}873 - \frac{11552}{T} - 22{\cdot}679 \ln T \quad .. \quad .. \quad .. \quad .. \quad (5)$$

Accordingly, the means taken over the three percentages of biuret are plotted to the regression equation (5) in Fig. 2.

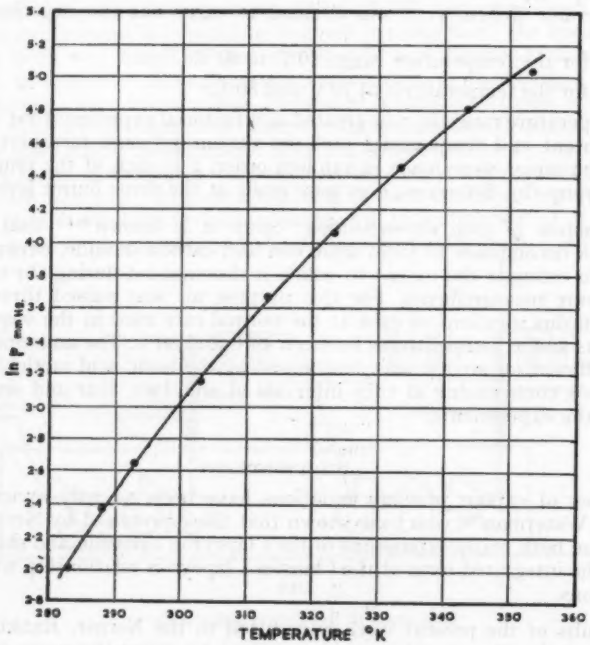

FIG. 2

Regression curve ln p $170{\cdot}873 - \frac{11552}{T} - 22{\cdot}679 \ln T$ from overall mean values

Experimental points ●

The results of the factorial experiment, based on the temperature range 10°C to 60°C, were used for analysis of variance. This showed that temperature caused a significant variation, which was to be expected, but the only significant difference due to biuret occurred between the 0·3% and 6·5% levels and this amounted to less than 5 mm Hg even at the highest temperatures.

Decomposition of urea: By assuming the urea decomposition to be represented by the overall equation,

$$CO(NH_2)_2+H_2O \rightleftharpoons CO_2+2NH_3,$$

the ammonia in the air stream after passing through the urea solution may be expressed as an "equivalent urea loss". The results of the ammonia evolution determinations are represented in this way in Fig. 3.

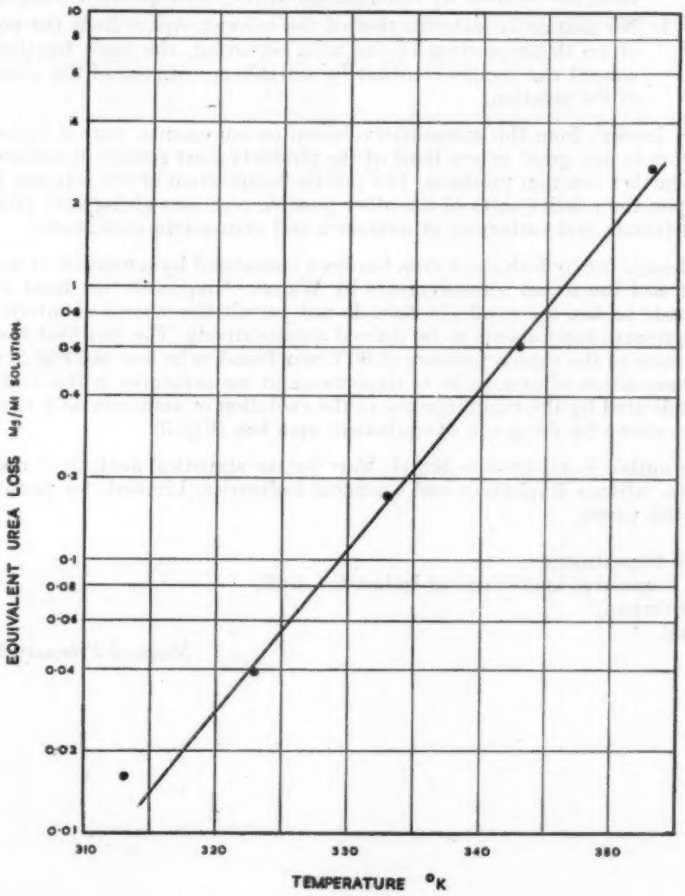

FIG. 3

Ammonia evolution from saturated aqueous solutions of urea as equivalent urea loss

From these results it can be seen that in the course of the vapour pressure experiments, the loss of urea as ammonia was small compared with the concentration of urea in the saturated solutions used. Other decomposition products which would remain in solution are possible and could, in consequence, influence the activity of the solvent.

One may consider the possible effects of such products as follows:

1. Increase in the mole fraction of the solvent. This may occur by association between solute molecules.
2. Decrease in the mole fraction of the solvent. This may be brought about by an increase in the effective moles of solute from decomposition of the urea to produce other molecular species. Also, water may be removed from the solution by combination in the decomposition reactions.
3. No change in mole fraction of the solvent. Apart from the possibility of no decomposition of the urea occurring, the mole fraction of the solvent can remain constant by suitable adjustment of the composition of the solution.

It is known, from the ammonia evolution measurements, that if hydrolysis of urea occurs to any great extent most of the products must remain in solution in the form of further reaction products. The precise composition of the solution then depends upon the relative rates of the other possible reactions giving such products as the bicarbonate and carbonate of ammonia and ammonium carbamate.

Although the hydrolysis of urea has been considered by a number of workers in the past and the recent measurements by Warner[11] represent the most extensive study made so far, the available data do not permit the system of interest in the vapour pressure experiments to be defined quantitatively. The fact that the experimental value of the vapour pressure at 80°C was found to be low (see Fig. 2) suggests the decomposition of urea to be of importance at temperatures in this region. This is also indicated by the rapid increase in the evolution of ammonia with rise in temperature, shown by the graph of equivalent urea loss (Fig. 3).

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